



NRL/MR/6360--17-9743

# **Extraction of Carbon Dioxide and Hydrogen from Seawater by an Electrolytic Cation Exchange Module (E-CEM) Part V: E-CEM Effluent Discharge Composition as a Function of Electrode Water Composition**

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August 1, 2017

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 01-08-2017		2. REPORT TYPE Memorandum Report		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE  Extraction of Carbon Dioxide and Hydrogen from Seawater By an Electrolytic Cation Exchange Module (E-CEM) Part V: E-CEM Effluent Discharge Composition as a Function of Electrode Water Composition				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)  Heather D. Willauer, Felice DiMascio, <sup>1</sup> and Dennis R. Hardy <sup>2</sup>				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 63-1C27-07	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Naval Research Laboratory, Code 6300 4555 Overlook Avenue, SW Washington, DC 20375-5320				8. PERFORMING ORGANIZATION REPORT NUMBER  NRL/MR/6360--17-9743	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Office of Naval Research One Liberty Center 875 North Randolph Street, Suite 1425 Arlington, VA 22203				10. SPONSOR / MONITOR'S ACRONYM(S)  ONR	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES  <sup>1</sup> Office of Naval Research (ONR), Arlington, VA <sup>2</sup> Nova Research Inc., Alexandria, VA					
14. ABSTRACT  A sea-based synthetic fuel process that combines carbon dioxide (CO <sub>2</sub> ) and hydrogen (H <sub>2</sub> ) to make jet fuel at sea is envisioned. However, before such a process can become feasible, methods must be developed to extract large quantities of CO <sub>2</sub> and H <sub>2</sub> from seawater fast and efficiently. An Electrolytic Cation Exchange Module (E-CEM) has been developed and extensively evaluated at a seawater flowrate of 0.5 gallons per minute (gpm) as a function of pH, current density, time, polarity reversal, and CO <sub>2</sub> and H <sub>2</sub> recovery. These evaluations have established E-CEM design parameters that are currently being used to scale-up and construct an E-CEM prototype capable of processing up to 25 gpm of seawater. This fifty time scale-up has led to the need to regulate E-CEM effluent discharge water composition with respect to pH and chlorine content. This report details the results of two separate evaluations of the E-CEM that specifically address changes in E-CEM performance and effluent concentrations with changes in influent electrode water composition and flowrate. These evaluations have identified additional software and hardware capabilities that will be included in the prototype skid to ensure E-CEM performance and operational safety while maintaining effluent water quality.					
15. SUBJECT TERMS Electrolytic Cation Exchange Module (E-CEM) Carbon dioxide Hydrogen Carbon capture					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT  Unclassified Unlimited	18. NUMBER OF PAGES  26	19a. NAME OF RESPONSIBLE PERSON Heather D. Willauer
a. REPORT Unclassified Unlimited	b. ABSTRACT Unclassified Unlimited	c. THIS PAGE Unclassified Unlimited			19b. TELEPHONE NUMBER (include area code) (202) 767-2673



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## EXECUTIVE SUMMARY

A sea-based synthetic fuel process that combines carbon dioxide (CO<sub>2</sub>) and hydrogen (H<sub>2</sub>) to make jet fuel at sea is envisioned. However, before such a process can become feasible, methods must be developed to extract large quantities of CO<sub>2</sub> and H<sub>2</sub> from seawater fast and efficiently. To this end, commercially available electrodeionization cells have been modified by NRL to function as electrolytic cation exchange modules (E-CEM). After the technology was successfully demonstrated in the laboratory, it was scaled-up and integrated into a mobile skid design. The skid was constructed and pre-tested at Havlovick Engineering Services in Idaho Falls, Idaho before it was sent to NRL Key West on January 21, 2011 to be evaluated in a marine environment. Over the course of six years the E-CEM performance has been extensively evaluated at a seawater flowrate of 0.5 gallons per minute (gpm) as a function of pH, current density, time, polarity reversal, and CO<sub>2</sub> and H<sub>2</sub> recovery. These evaluations have established E-CEM design parameters that are currently being used to scale-up and construct an E-CEM prototype capable of processing up to 25 gpm of seawater. This fifty time scale-up in E-CEM processing along with changes in electrode influent water composition that will be used for the new prototype have led to the need to regulate E-CEM effluent discharge water composition with respect to pH and chlorine content. This report details the results of two separate evaluations (February and April of 2017) of the E-CEM that specifically address changes in E-CEM performance and effluent concentrations with changes in influent electrode water composition and flowrate. These evaluations have identified additional software and hardware capabilities that will be included in the prototype skid to ensure E-CEM performance and operational safety while maintaining effluent water quality.

# **EXTRACTION OF CARBON DIOXIDE AND HYDROGEN FROM SEAWATER BY AN ELECTROLYTIC CATION EXCHANGE MODULE (E-CEM) PART V: E-CEM EFFLUENT DISCHARGE COMPOSITION AS A FUNCTION OF ELECTRODE WATER COMPOSITION**

## **1.0 BACKGROUND**

The Naval Research Laboratory (NRL) is developing the technologies to produce operational fuel from environmental carbon dioxide (CO<sub>2</sub>) and hydrogen (H<sub>2</sub>) on land and at sea to enhance Navy combat capability and provide greater energy security. Synthesizing drop in replacements for petroleum-derived fuel at or near the point of use translates into “Freedom of Action for the Warfighter.” This potential “game changing” proposition could offer the Navy significant logistical, operational, and cost advantages by reducing dependence on foreign sources of fuel, minimizing fuel logistic tails and their vulnerabilities, maximizing warfighting efforts, and meeting alternative energy goals set forth by SECNAV. These goals require that 50 percent of DON energy requirements at sea and on shore be derived from alternative (non-petroleum) resources by 2020. These goals seek to enhance combat capabilities and provide greater energy security while having a minimal impact on the environment.

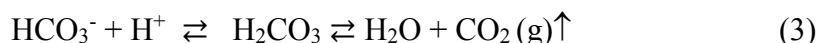
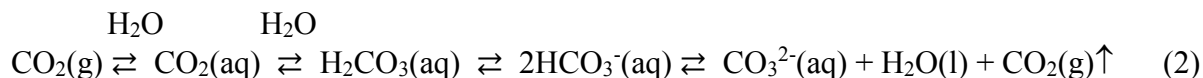
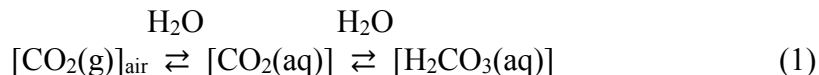
Technologies currently exist to synthesize hydrocarbon fuel on land given sufficient primary energy resources such as coal, natural gas, or biomass [1,2]. The Navy is currently certifying naval engines to operate on alternative fuels from land-based resources (i.e. algae, camelina, switch grass, coal liquids, and natural gas to liquids). However, these resources are not practical for remote littoral locations or sea-based operations since the resources must be delivered from land to the point of use.

Through the current support of NRL’s 6.1 basic research program and OPNAV N45, NRL continues to conduct the sustained basic and applied research necessary to develop the chemistries required to produce alternative low carbon liquid fuel from feedstocks found in seawater using electricity as the primary energy source. Developing the technologies to extract CO<sub>2</sub> from seawater is part of a larger project to synthesis drop in replacement fuel for petroleum-derived fuel on land or at sea [3-11].

In 2009 NRL re-configured a commercial chlorine dioxide generation module to function as an electrolytic cation exchange module (E-CEM) for the purposes of exploiting seawater’s pH as an indirect approach to recovery of CO<sub>2</sub> in the form of bicarbonate and carbonate from seawater. The novel hybrid process takes advantage of Continuous electrodeionization (CEDI) electroregeneration mechanisms and ion transport properties to control and reduce seawater pH [3-6, 8, 9]. Simultaneously, the process produces hydrogen gas through electrolytic dissociation of water in the cathode compartment [3-6, 8, 9].

Exploiting seawater’s pH is an indirect approach to recovery of CO<sub>2</sub> in the form of bicarbonate from the equilibrium conditions of CO<sub>2</sub> in seawater as shown in equations 1 and 2 [12]. The protons generated in the process acidify the seawater from pH 7.8 to pH 6.0. Johnson, et al demonstrated that when the pH of seawater is decreased to 6 or less, carbonate and bicarbonate

are re-equilibrated to CO<sub>2</sub> gas as shown in equation 3. This method has been the basis for standard quantitative ocean [CO<sub>2</sub>]<sub>T</sub> measurements for over 25 years [12].



NRL transitioned the technology from the laboratory to a marine environment for the purpose of scaling-up and integrating processes. In this environment at the larger scale the E-CEM was evaluated continuously under different operating conditions that led to improvements in process efficiencies and module design. As a result NRL along with commercial partners has successfully designed and developed an E-CEM prototype that is capable of producing more than enough feedstock (CO<sub>2</sub> and H<sub>2</sub>) to produce a gallon per day of liquid hydrocarbon. This fifty time scale-up in E-CEM seawater processing along with changes in electrode water composition that will be used for the new prototype have led to this test series. These test are directed at assessing E-CEM performance as a function of different water composition and understanding and controlling E-CEM effluent discharge water composition with respect to pH and chlorine content. These data will be used to ensure E-CEM prototype system performance and discharge compliance.

## 2.0 OBJECTIVE

The objective of these evaluations is to determine the effects of using different water compositions fed to the electrode compartments of the E-CEM. A reverse osmosis (RO) system is currently used to supply the electrodes with water. The following key technical challenges associated with changing the RO water supply to Key West-city water on the E-CEM performance are addressed in this test series:

- E-CEM effluent discharge pH
- Anode effluent chlorine content
- Cathode effluent pH
- E-CEM process electrical efficiency

## 3.0 APPROACH

In these test series an E-CEM carbon capture skid was operated at NRL's Marine Corrosion Facility in Key West, Florida two separate occasions (February and April of 2017) to evaluate the performance of the E-CEM using KW city water as the electrode influent.

## 4.0 TEST DESCRIPTION

### 4.1 E-CEM

A custom built E-CEM was used for this evaluation. Figure 1 provides a schematic of a typical three compartment module configuration that details the major components of the module and the primary reactions that occur in each of the compartments of the module.

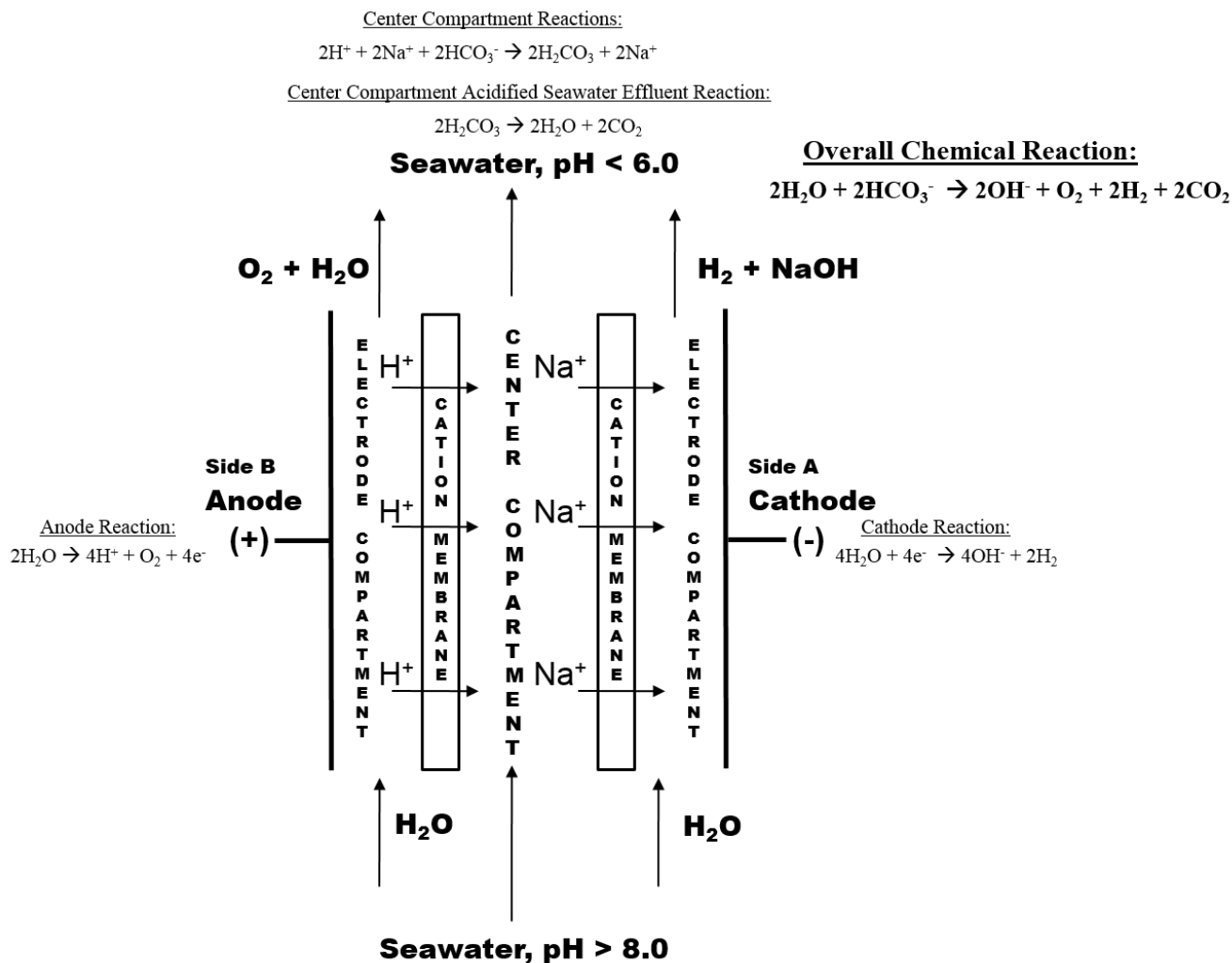


Figure 1. Schematic of Electrochemical Acidification Cell

The major components of the E-CEM include a central compartment, electrode compartments (cathode and anode) and cation-permeable membranes which separate the three compartments. A cation-permeable membrane is a cross-linked polymer backbone with sulfonic acid groups attached. The acid functionality provided discrete channels for cations to migrate through the polymer matrix while blocking the passage of anions.



The E-CEM in Figure 1 uses direct current (DC) to exchange sodium ions ( $\text{Na}^+$ ) for  $\text{H}^+$  ions in a central stream that is flowing adjacent to two cation exchange membranes. Seawater is passed through the center compartment of the three compartment cell.  $\text{Na}^+$  ions are transferred through the membrane closest to the cathode and removed from the seawater by means of direct current (DC) voltage. These  $\text{Na}^+$  ions are replaced by  $\text{H}^+$  ions as the current drives the ions through the membrane closest to the anode to acidify the seawater.

Table 1. E-CEM Configuration

<b>Dimensions</b>	
Approximate Overall Cell Dimension	33 cm x 61 cm x 16 cm
Center Compartment Width	14 cm
Center Compartment Height	35.5 cm
Center Compartment Thickness	0.90 cm
Center Compartment Volume	447 $\text{cm}^3$
Membranes Active Area	497 $\text{cm}^2$ (each)
Each Electrode Compartment Volume	14.4 $\text{cm}^3$
<b>Electrical Specification</b>	
Electrode Active Area	497 $\text{cm}^2$ (each)
Max. Current Density	1,500 $\text{A m}^{-2}$
<b>Flow Specification</b>	
Max. Seawater Flow Rate	3900 mL/min
Operating Seawater Flow Rate	1900 mL/min
Max. RO Electrolyte Flow Rate	2100 mL/min
Operating RO Flow Rate	230 mL/min
Max. Operating Temperature	60 $^{\circ}\text{C}$
Max. Operating Pressure	350 kPa
<b>Materials</b>	
Anode	Platinized Titanium
Cathode	Platinized Titanium
Membrane	Ionpure Cation-Permeable Membrane
Molded Frame and End Block	Polyethylene (PE)

In the cell, the anolyte is the water fed to the anode compartment. At the anode  $\text{H}^+$  is generated and it must migrate from the surface of the anode, through the cation-permeable membrane, and into the center compartment where it replaces  $\text{Na}^+$ . Therefore the anolyte was diluted such that  $\text{H}^+$  ions are in excess and do not compete with any other cations.

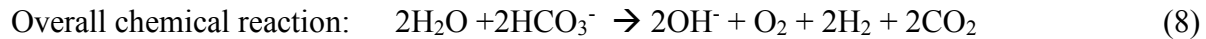
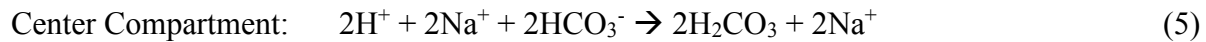
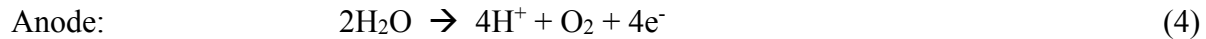
The catholyte is the water fed to the cathode compartment and it must be free from hardness ions such as calcium ( $\text{Ca}^{+2}$ ) and magnesium ( $\text{Mg}^{+2}$ ). The pH in the cathode compartment is high enough to precipitate these hardness ions. Therefore, a total hardness concentration of less than 50 ppm is desired.

Water produced from a reverse osmosis (RO) system has been normally used in these evaluations. In these test series the RO water will be replaced with KW-city drinking water and the effects on module performance, anode and cathode effluent discharge, and anode effluent chlorine discharge are primary objectives of this evaluation.

Table 1 provides a detailed description of the E-CEM's electrical and flow rate specifications along with the materials used in the cell configuration. The anode and cathode are platinum plated titanium electrodes. These tests determined the flow rate to current ratio required to lower seawater pH to the target level. This information determines electrode performance and operating life. The cell contained a polyethylene extruded cation permeable membrane. Membrane performance was evaluated during these tests, since its performance and operating life is based on current density and level of organic compounds contained in the seawater.

## 4.2 E-CEM Reactions

Figure 1 shows a continuous flow process in which seawater is passed through the center compartment of the E-CEM at a flow rate of 0.5 gal/min. The  $\text{Na}^+$  in the seawater are exchanged for  $\text{H}^+$  produced by the stream that is flowing adjacent to two cation-permeable membranes. Direct current (DC) facilitates this exchange. The principle chemical reactions within the E-CEM are simplified as shown in eqs 4 - 8.



The amount of  $\text{H}^+$  generated by the anode is proportional to the applied electrical current, which follows Faraday's law. The anode and cathode reactions used to theoretically determine the amount of  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2$ , and  $\text{O}_2$  produced per amp-second of current passed through the electrodes are provided in eqs 9-14 as follows:

For the anode reaction, 96,487 A-sec will produce  $\frac{1}{4}$  mole  $\text{O}_2$  gas and 1 mole  $\text{H}^+$  and for the cathode reaction, 96,487 A-sec will produce  $\frac{1}{2}$  mole  $\text{H}_2$  gas and 1 mole  $\text{OH}^-$ . This allows the amount of  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2$ , and  $\text{O}_2$  produced per amp/second of current passed through the electrodes to be derived:

### Anode Reaction

$$\left(\frac{1/4 \text{ mole O}_2}{96,487 \text{ A} \cdot \text{sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000155 \frac{\text{mole O}_2}{\text{A} \cdot \text{min}} \quad (9)$$

$$\left(\frac{1 \text{ mole H}^+}{96,487 \text{ A} \cdot \text{sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000622 \frac{\text{mole H}^+}{\text{A} \cdot \text{min}} \quad (10)$$

### Cathode Reaction

$$\left(\frac{1/2 \text{ mole H}_2}{96,487 \text{ A} \cdot \text{sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000311 \frac{\text{mole H}_2}{\text{A} \cdot \text{min}} \quad (11)$$

$$\left(\frac{1 \text{ mole OH}^-}{96,487 \text{ A} \cdot \text{sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000622 \frac{\text{mole OH}^-}{\text{A} \cdot \text{min}} \quad (12)$$

Therefore, for seawater with a bicarbonate ( $\text{HCO}_3^-$ ) ion concentration of 142 ppm (0.0023 M) at a planned operating flow rate of 0.5 gal/min (1900 mL/min), a theoretical applied current of 7.0 amps will be required to lower the pH to less than 6.0 and convert  $\text{HCO}_3^-$  to carbonic acid ( $\text{H}_2\text{CO}_3$ ) (equation 13).

$$\frac{\left(\frac{0.0023 \text{ mole HCO}_3^-}{\text{Liter}}\right)\left(\frac{1.89 \text{ Liter}}{\text{min}}\right)}{\left(\frac{0.000622 \text{ mole H}^+}{\text{A} \cdot \text{min}}\right)} = 7.0 \text{ A} \quad (13)$$

Removal efficiency can be defined as the ratio of the theoretical amount of  $\text{CO}_2$  removed to the actual amount of  $\text{CO}_2$  removed in the acidified seawater. The theoretical amount of  $\text{CO}_2$  that can be removed from the acidified seawater is 0.0023 moles per liter. Removal efficiencies are never 100 % and can range from 50 to 95 % based on various unit operating requirements. The overall removal of  $\text{CO}_2$  in these tests was measured to be approximately 92%.

The amount of  $\text{H}_2$  gas generated at 7.0 A is

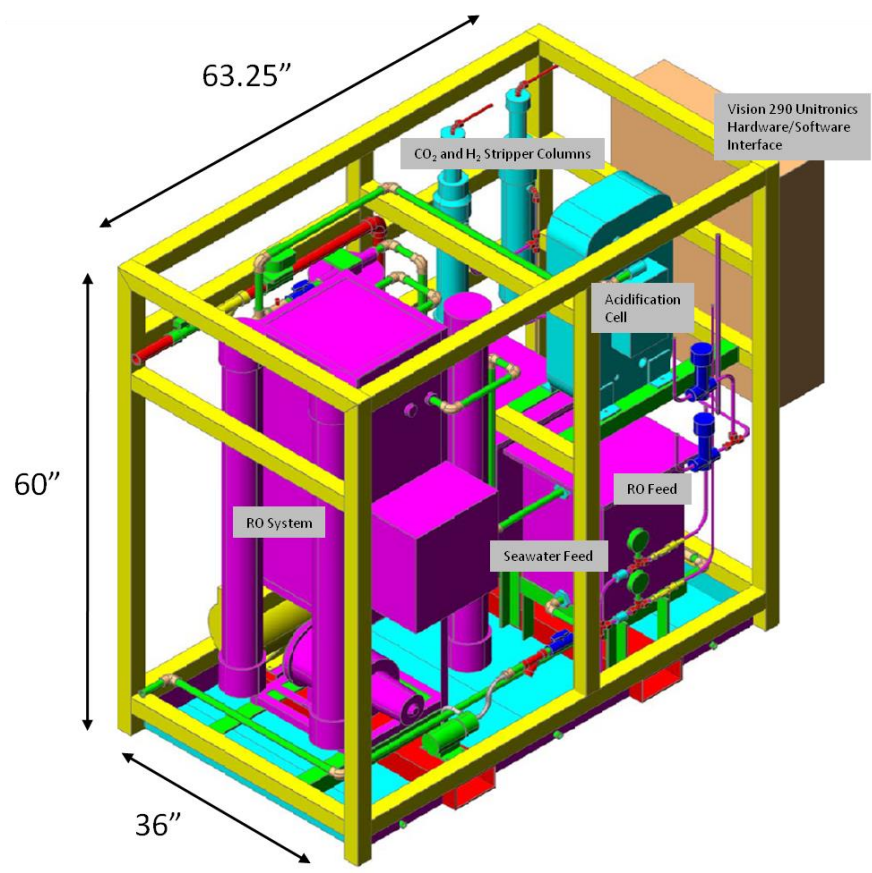
$$\left(\frac{1/2 \text{ mole H}_2}{96,487 \text{ A} \cdot \text{sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right)(7.0 \text{ A}) = 0.0022 \frac{\text{mole H}_2}{\text{min}} \quad (14)$$

Under these conditions, the molar ratio of  $\text{H}_2$  to  $\text{CO}_2$  is 0.73. Increasing the current increases the molar ratio of hydrogen to carbon dioxide with no effect on the operation of the module.  $\text{H}^+$

generated will either exchange with  $\text{Na}^+$  in the seawater to further lower its pH or migrate through the center compartment and into the cathode compartment where it will combine with  $\text{OH}^-$  to form water.

### 4.3 Carbon Capture Skid

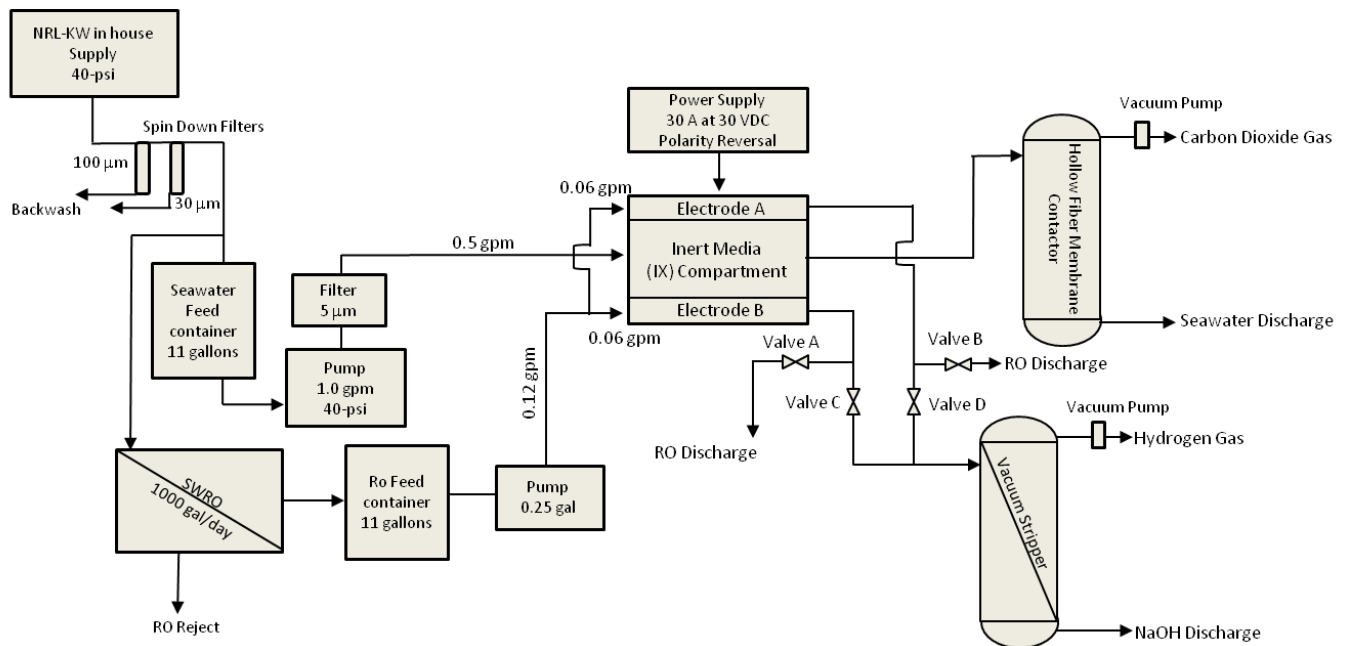
The E-CEM was mounted onto a portable skid along with an RO unit, power supply, pump, carbon dioxide recovery system, and hydrogen stripper to form a carbon capture system. Figures 2 and 3 are a composite schematic and picture of the system with dimensions of 63" x 36" x 60". Figure 4 provides a block diagram that describes how the system in Figure 2 operates.



**Figure 2. Composite Schematic of Carbon Capture Skid**



**Figure 3a. Front and 3b. Back Pictures of Carbon Capture Skid at NRL Key West Facility**



**Figure 4. Block Diagram Carbon Capture Skid**

The system has evolved since its initial conception and installation at NRL Key West in January of 2011, to include different carbon recovery technology and more filtration media. Seawater is supplied to the skid by an in house 40 psi supply line. The water is filtered by two spin down filters in series (100  $\mu\text{m}$  and 30  $\mu\text{m}$ ). After filtration a portion of the seawater is sent to an 11 gallon high density polyethylene container that functions as the seawater feed container. Before the seawater in the seawater feed tank is fed to the center compartment of the E-CEM at 0.5 gallon/minute, it is pumped through a 5  $\mu\text{m}$  filter cartridge. The other portion of the seawater supply is fed to the RO system for processing. The RO system is an EPRO-1000SW from Crane Environmental, Inc. (Venice, FL) that is capable of producing 0.07 gallons per minute (1000 gallons per day) of permeate (potable water quality from seawater at a conductivity of approximately 200  $\mu\text{S/cm}$ ). This water is stored in an 11 gallon polyethylene container that is specified as the RO feed container (Figures 2-4). This water is the feed water to the electrode compartments of the E-CEM at a flow rate of 0.12 gallon/minute (460 ml/min). The flow is split as it enters the E-CEM resulting in electrode compartment flow rates of 0.06 gallon/minute (230 mL/min). In this evaluation the RO water to the electrodes will be replaced by KW-city water to determine how its composition effects E-CEM performance and effluent discharge.

Figure 4 shows that the E-CEM has been designed so that the polarity of the cell can be reversed. This reversal is essential to aid in reducing mineral deposits on the electrode that is operating as the cathode. Ions that impart hardness to seawater include calcium ( $\text{Ca}^{+2}$ ) and magnesium ( $\text{Mg}^{+2}$ ) ions, and their total concentration is typically less than 2,000 mg/L. Hardness ions can migrate from the seawater in the center compartment (Figures 1 and 4) or could be introduced into the cathode compartment by the water feeding the cathode compartment. In previous laboratory studies deionized water was used as the feed water to the cathode compartment, so the only hardness ions entering the cathode compartment were from the center compartment [3,5]. However, during these tests it was found that the electrical resistance (voltage divided by amperage) increased from 4.07 Ohms to 6.45 Ohms over 150 minutes of operation. This 58% increase in resistance was an indication that minerals ( $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ ) were depositing on the electrode surface of the cathode. These effects can be reduced by reversing the polarity of the electrodes. The change in polarity causes the minerals (scaling) to disassociate from the electrode surface. This is a common practice in Electrodialysis Reversal (EDR) processes. These processes are used to desalinate brackish ground and surface waters. Figure 4 shows that the flow from the individual electrode compartments to the hydrogen stripper are controlled by solenoid valves (valves C and D) to accommodate the necessary changes in polarity to the cell.

A Mastech HY3030EX 0-30 amp, 0-30 volt high-current, high-voltage regulated DC power supply controls the pH of the seawater. NRL's Marine Corrosion Facility supplied two (220 Vac, 40 A) and four (110 Vac, 20 A) to power the skid, and a continuous supply of Key West seawater.

## **5.0 EXPERIMENTAL**

### **5.1 Carbon Capture Skid Operating Conditions**

Table 2 provides the operating flow rate conditions for the acidification cell in these test series. Seawater flows through the center compartment of the cell at 0.5 gal/min (1900 mL/min) (Figures 1 and 4). The Table shows that at this flow rate the maximum calculated  $\text{CO}_2$  available

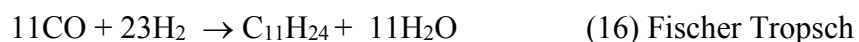
for extraction is 0.004 moles/min (0.0023 moles/L CO<sub>2</sub> (100 mg/L) x 1.89 L/min). The RO flow rate to the electrode compartments is 0.06 gal/min (230 mL/min).

Table 2. E-CEM Operating Configuration

Applied Current to Electrochemical Cell	7 amps	30 amps
<b>Operating Seawater Flow Rate Center Compartment</b>	<b>0.5 gal/min</b>	<b>0.5 gal/min</b>
CO <sub>2</sub> Concentration Extracted at 100% efficiency (eq 13)	0.0040 moles/min	0.0040 moles/min
CO <sub>2</sub> Concentration Extracted at 92% efficiency (eq 13)	0.0037 moles/min	0.0037 moles/min
<b>Operating RO Flow rate to Electrode Compartments</b>	<b>0.06 gal/min</b>	<b>0.06 gal/min</b>
H <sub>2</sub> Concentration Extracted at 100% (eq 14)	0.002 moles/min	0.010 moles/min
<b>Calculated Synthetic Fuel for 100% CO<sub>2</sub> and H<sub>2</sub></b>		0.027 gal/day

In these test series a 30 volt, 30 amp DC power supply is used to provide current to the acidification cell. Table 2 provides the operating flow rates and currents that were evaluated in the different test series and the calculated minimum amounts of CO<sub>2</sub> and H<sub>2</sub> extractable at those currents and process efficiencies of 92% and 100%. The Table shows that the maximum calculated extractable CO<sub>2</sub> when the module is operating at 92% efficiency and 7 amps is 0.0037 moles/min. Thus the theoretical flow rate in mL/min to current ratio is estimated to be 270 mL/amp (equation 13). The available hydrogen at 7 amps is 0.002 moles/min. At these hydrogen concentrations, a mole ratio of 0.5:1 H<sub>2</sub> to CO<sub>2</sub> is inefficient for hydrocarbon production. The module was operated during these evaluations over a range of current density to establish relationships for module performance using KW-city water as the electrode source.

There are two principle reactions that take place in the synthesis of a jet fuel fraction (C<sub>11</sub>H<sub>24</sub>) from CO<sub>2</sub> and H<sub>2</sub>. In equation 14, CO<sub>2</sub> is reduced to CO by the reverse water gas shift reaction. Then CO is converted to a theoretical minimum hydrocarbon chain length of eleven by the Fischer-Tropsch reaction shown in equation 15 [13]. The sum of equations 15 and 16 result in equation 17. Equation 17 shows the mole ratio of H<sub>2</sub> to CO<sub>2</sub> is 3.1 to 1, and laboratory results indicate that this ratio is necessary for efficient hydrocarbon production.



To produce feedstock ratios of 3:1 for future hydrocarbon production the current to the cell has to be increased over 4 times to 30 amps. At this current the hydrogen concentration will increase to 0.01 moles/min (equation 13), and the current to flow rate ratio will be decreased from 270 mL/amp to 63 mL/amp. From equations 14 through 16 and the calculated moles/min of CO<sub>2</sub> and H<sub>2</sub> given in Table 2 when the cell is operating at 30 amps, the maximum amount of synthetic

$C_{11}H_{24}$  that could theoretically be produced in this apparatus is 0.03 gallons/day ( $2 \times 10^{-5}$  gallons/minute or 4.5 mL/hour).

The E-CEM was operated at a recovery of 81%. The term “recovery” is used to define the ratio of product quantity (influent seawater flow rate, Table 2) over the total feed quantity to the cell (influent seawater flow rate and influent deionized flow rate, Table 2) as a percent. A high recovery allows the size of the filtration unit along with the energy requirements for the unit to be minimized. This high recovery is possible due to the RO system and the ability to change the polarity of the electrodes in efforts to reduce scaling on the electrodes from hardness ions.

## **5.2 Carbon Dioxide and Hydrogen Gas Analysis**

A UIC Coulometric system (UIC Inc, Joliet, IL 60436) [12] was used to measure the  $[CO_2]_T$  content of the seawater throughout these tests. The  $[CO_2]_T$  content of the seawater before acidification was measured to be approximately 100 mg/L.

A Honeywell 7866 digital gas analyzer with a thermal conductivity detector was used to measure the amount of  $H_2$  gas from the stripper column throughout the different tests.

## **5.3 Seawater pH**

The seawater pH was monitored continuously using a standard combination electrode as it exits the  $CO_2$  center compartment of the cell. The seawater pH changes as a function of current applied to the E-CEM.

## **5.4 SAFETY**

Safety is paramount in all field operations. Since hydrogen was produced during these test series, it was constantly diluted with air below its lower flammability and explosive limit.

## **6.0 RESULTS AND DISCUSSION**

The NRL team operated the E-CEM carbon capture skid to evaluate, measure, and optimize the system’s performance using KW-city water in the electrode compartments. This analysis concentrates on the E-CEM performance during two separate evaluations (February and April of 2017) as a function of current density, pH, time, polarity reversal, and E-CEM effluent discharge pH, anode effluent chlorine content, cathode effluent pH, and E-CEM process electrical efficiency. These data provide insight towards identifying and mitigating any environmental challenges that could arise during operation of NRL’s future prototype E-CEM that will process over 25 gpm of seawater at the NRL-KW facility.

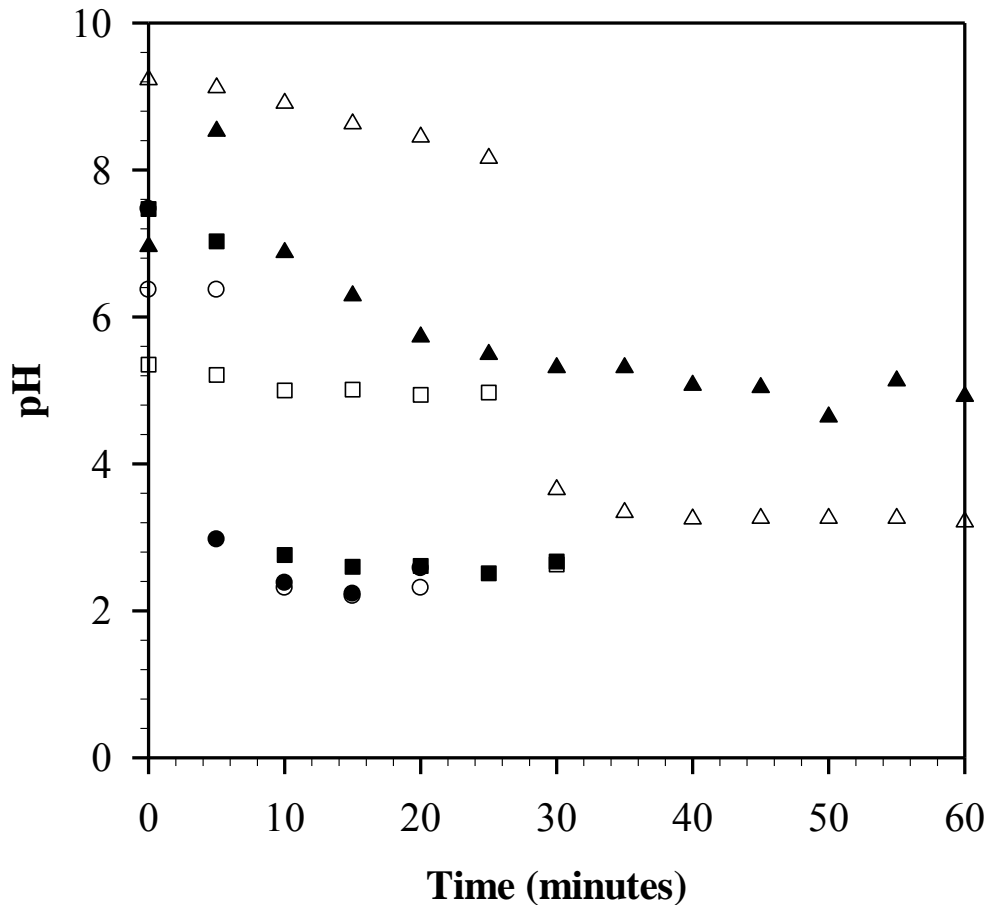
### **6.1 E-CEM Effluent Discharge and Performance**

Several experiments were performed to characterize the combined effluent and individual effluent streams (anolyte, seawater, and catholyte) from operation of the E-CEM carbon capture skid under various operating conditions using RO and KW-city water in the electrode compartments.



### 6.1.1 E-CEM Performance and Effluent pH as a Function of Electrode Water Source

Figure 5 compares the pH profiles of six polarity cycles as a function of time and current density (612, 408, 204 Amps/cm<sup>2</sup>) using RO (closed symbols) and KW-city water (open symbols) in the electrode compartments. The figure shows that as previously reported the pH takes longer to fall below 6 as the applied current is decreased to the E-CEM. When 408 Amps/cm<sup>2</sup> of current density is applied to the module using KW-city water in the electrode compartments, the pH of the effluent seawater is still above 4.5 after twenty minutes of operation. At pH of 4.5 and below all the bicarbonate and carbonate in the seawater exist as carbonic acid and can be removed as CO<sub>2</sub> gas [12].

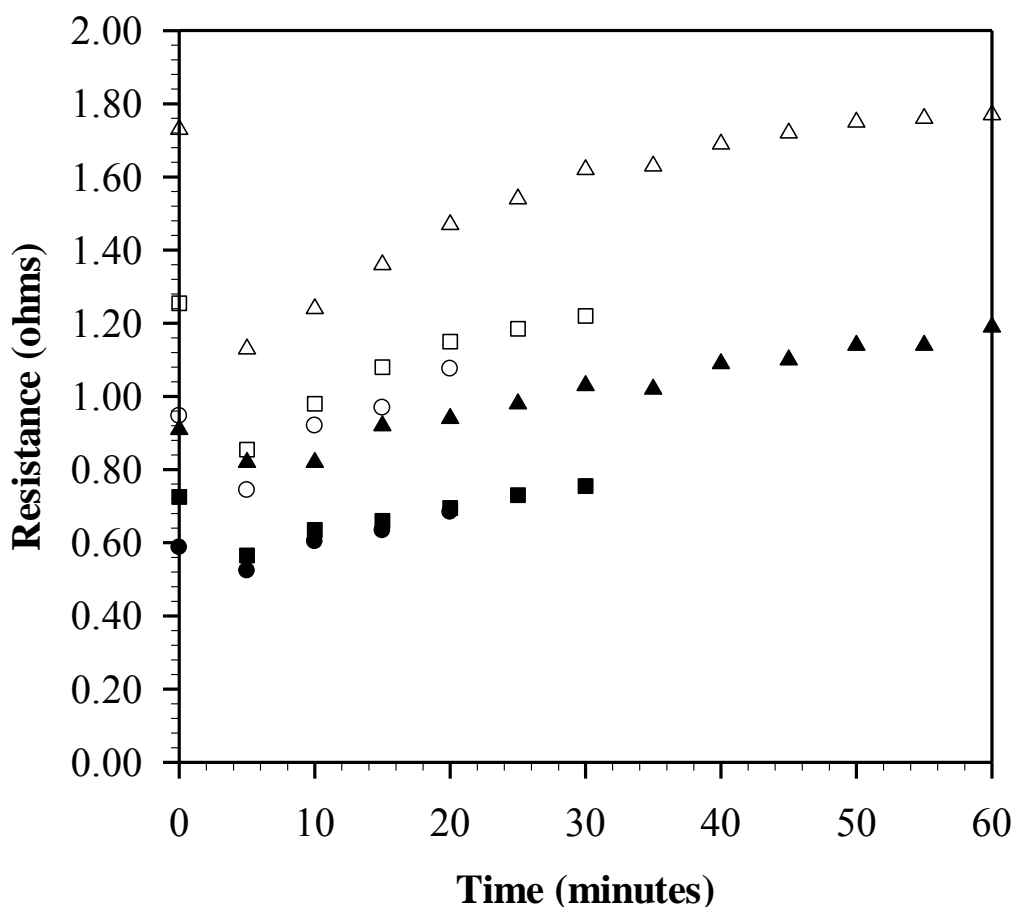


**Figure 5. A pH profile comparison for 6 polarity cycles measured at different applied current densities of, 612 Amps/m<sup>2</sup> 20 minute cycle, polarity A (●) RO electrode water source and polarity B (○) KW-city water electrode water source; 408 Amps/m<sup>2</sup> 30 minute cycle, polarity A (■) RO and polarity B (□) KW-city water; 204 Amps/m<sup>2</sup> 60 minute cycle, polarity A(▲) RO and polarity B (Δ) KW-city water.**

When the electrode water is switched to RO the pH of the seawater reaches 2.97 in five minutes. This figure shows a difference in E-CEM performance between the cycles using RO water and

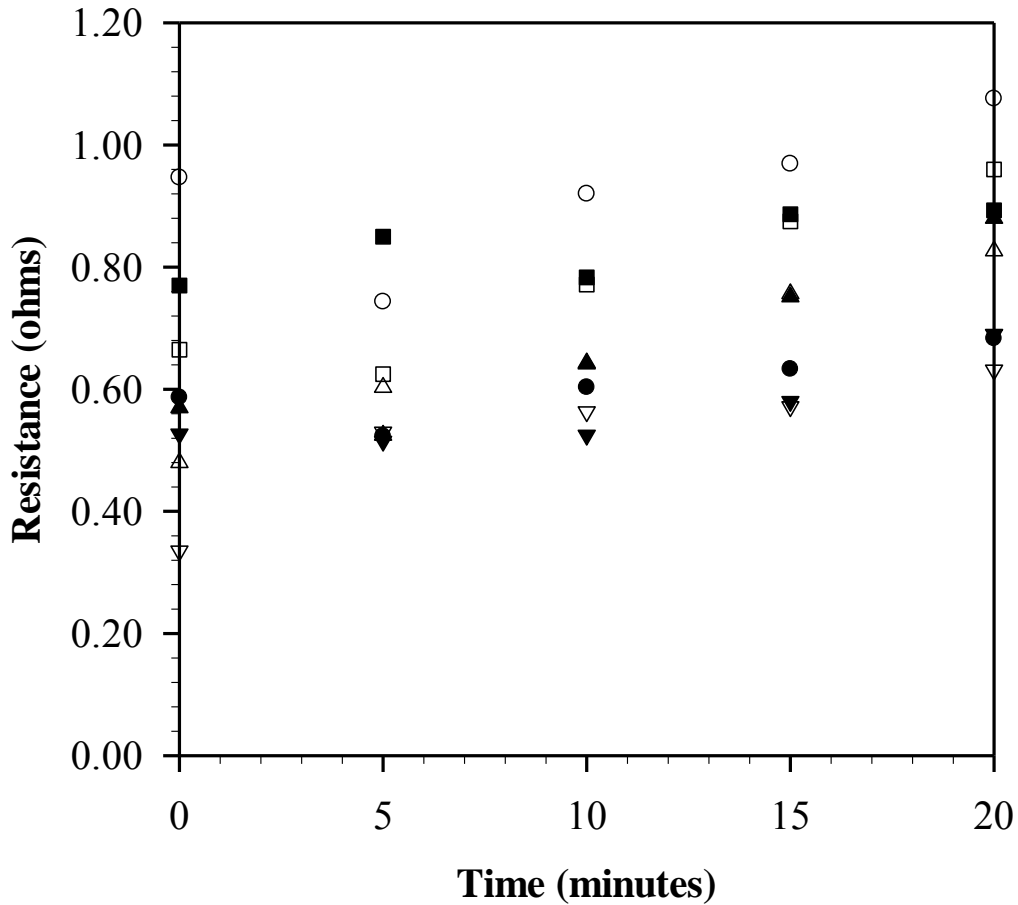
those using KW-city water and this difference is greater as less current is applied to the module. The changes in module performance between using RO and city water are attributed to the differences in water conductivity as the RO water measures 2,000 uS/cm and KW-city measures 340 uS/cm.

The significant difference in conductivity between KW-city water and RO water also leads to a significant effect on the module's electrical efficiency. Figure 6 shows that independent of current density applied to the module the average resistance in the module over time is 36% higher when KW-city water is used in the electrode compartments. The flowrate to each electrode compartment was initially set to 60 gpd (0.04 gpm).



**Figure 6. A resistance profile comparison for 6 polarity cycles measured at different applied current densities of, 612 Amps/m<sup>2</sup> 20 minute cycle, polarity A (●) RO electrode water source and polarity B (○) KW-city water electrode water source; 408 Amps/m<sup>2</sup> 30 minute cycle, polarity A (■) RO and polarity B (□) KW-city water; 204 Amps/m<sup>2</sup> 60 minute cycle, polarity A (▲) RO and polarity B (△) KW-city water.**

To improve the electrical efficiency of the module at the highest applied current density  $612 \text{ A/m}^2$ , the flowrate of water to the electrode compartments was reduced from 60 gpd to 9 gpd. Figure 7 compares the electrical resistance as a function of time and flowrate using RO and KW-city water in the electrode compartments. As the flowrate decreases from 60 gpd to 9 gpd the electrical resistance decreases in the module. At the lower operating flowrates the module performance using the Key West-city water in the electrode compartments is similar to operating the module with RO water. While these initial evaluations have verified previous trends associated with flowrate reduction to the electrode compartments, the precise role flowrate and water conductivity have on the modules performance still needs to be determined.



**Figure 7. Average resistance profiles measured at an applied current density of  $612 \text{ A/m}^2$  as a function of time and flowrate to the anode compartment, 60 gpd (●) RO electrode water source (○) KW-city water electrode water source; 30 gpd (■) RO water (□) KW-city water; 15 gpd (▲) RO water (△) KW-city water; and 9 gpd (▼) RO water (▽) KW-city water.**

Recycling the anode compartment is another potential way to increase the conductivity of the water in the anode compartment and enhance module performance using KW-city water. After one twenty minute polarity cycle the water from the anode compartment was continuously recycled over the next six polarity cycles that lasted fifteen minutes. The evaluation found the anolyte reached equilibrium after two polarity cycles as the average resistance in the module became consistent at 0.6 ohms and the conductivity of the anolyte measured an average of 840  $\mu\text{S}/\text{cm}$ . This increases the water conductivity by almost 60%.

Equations 4-8 show that  $\text{CO}_2$  in the form of bicarbonate and carbonate is removed from seawater and replaced with a strong hydroxide base to produce a combined water solution having a pH that can be or is greater than or equal to the original seawater solution. The average salinity and pH of KW seawater measures the same on an annual basis. However the pH has measured as low as 7.78 in June and as high as 8.3 in April (Table 3) during E-CEM evaluations.

Table 3. Electrochemical Acidification Cell Operating Configuration

Date of Measurement	Solution	pH
April 2016	Seawater	8.3
April 2016	Combine Effluent from E-CEM	9.3
June 2016	Seawater	7.8
June 2016	Combine Effluent from E-CEM	9.0 to 9.1
February 2017	Seawater	-
February 2017	Combine Effluent from E-CEM	9.7 to 10

This significant pH change along with difference in pH between the RO water (pH= 8.08) and the KW-city water (pH= 9.28) will influence the overall combined effluent discharge pH from the E-CEM. Table 3 compares the E-CEM effluent pH during three separate E-CEM evaluations. The Table shows that on average the effluent discharge is 1 to 1.2 pH units higher than the initial seawater fed to the E-CEM. The highest recorded was pH=10 and very little change in effluent pH was measured using KW-city water verses RO water as the electrode feed. Since seawater pH and salinity effect the overall effluent discharge from the E-CEM further operational parameters will be characterized to identify future operating standards to ensure that the prototype E-CEM combined effluents meet both the Federal and Florida State discharge pH limit of 9.5.

Experimental methods are currently being evaluated that have brought the pH of the cathode effluent down by as much as 0.3. The effect on the overall effluent discharge will be the subject of short term future evaluations.

#### 6.1.2 E-CEM Free Chlorine Effluent as a Function of Electrode Water Source

The anolyte and catholyte waters fed to the electrode compartments of the E-CEM located at NRL-KW has always been produced from an RO system. Key West-city water will be used as the anolyte and catholyte for the prototype E-CEM. Typically city drinking water can contain up to 4.0 mg/L of free chlorine. Free chlorine is defined as residual chlorine present in water as

dissolved gas ( $\text{Cl}_2$ ), hypochlorous acid ( $\text{HOCl}$ ), and or hypochlorite ion ( $\text{OCl}^-$ ). Both city water and RO will contain chloride ions and these chloride ions will oxidize at the anode to produce more free chlorine as shown in eq. 18

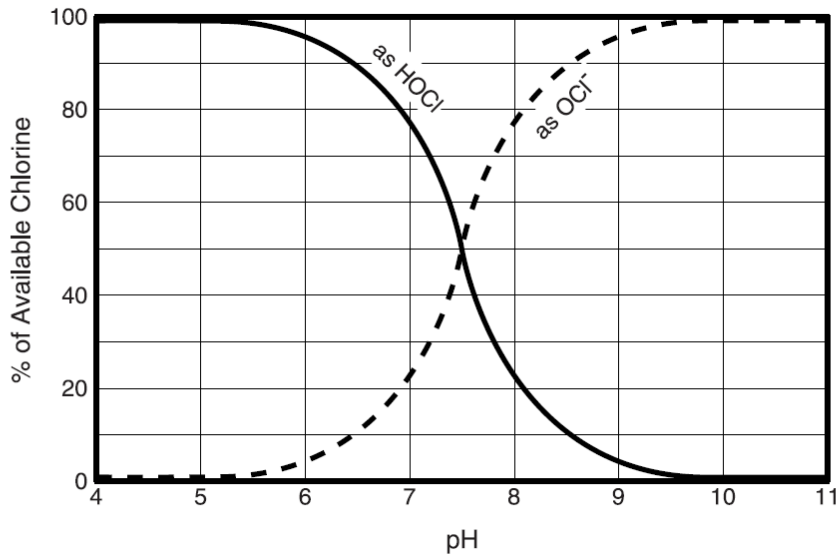


Free chlorine is responsible for causing necrosis in fish and as a result the maximum daily chlorine content of seawater must be 0.5 mg/L. The state of Florida's chlorine discharge limit into the ocean is 0.01 mg/L. These evaluations will quantify any amount of free chlorine ( $\text{Cl}_2$ ) produced by the operation of the E-CEM using KW-city water so that solutions are implemented to ensure effluent from the new prototype E-CEM meets Florida's discharge requirements.

Equation 19 shows how free chlorine formed from the oxidation of chloride (eq. 18) at the anode reacts with water to produced hypochlorous acid:



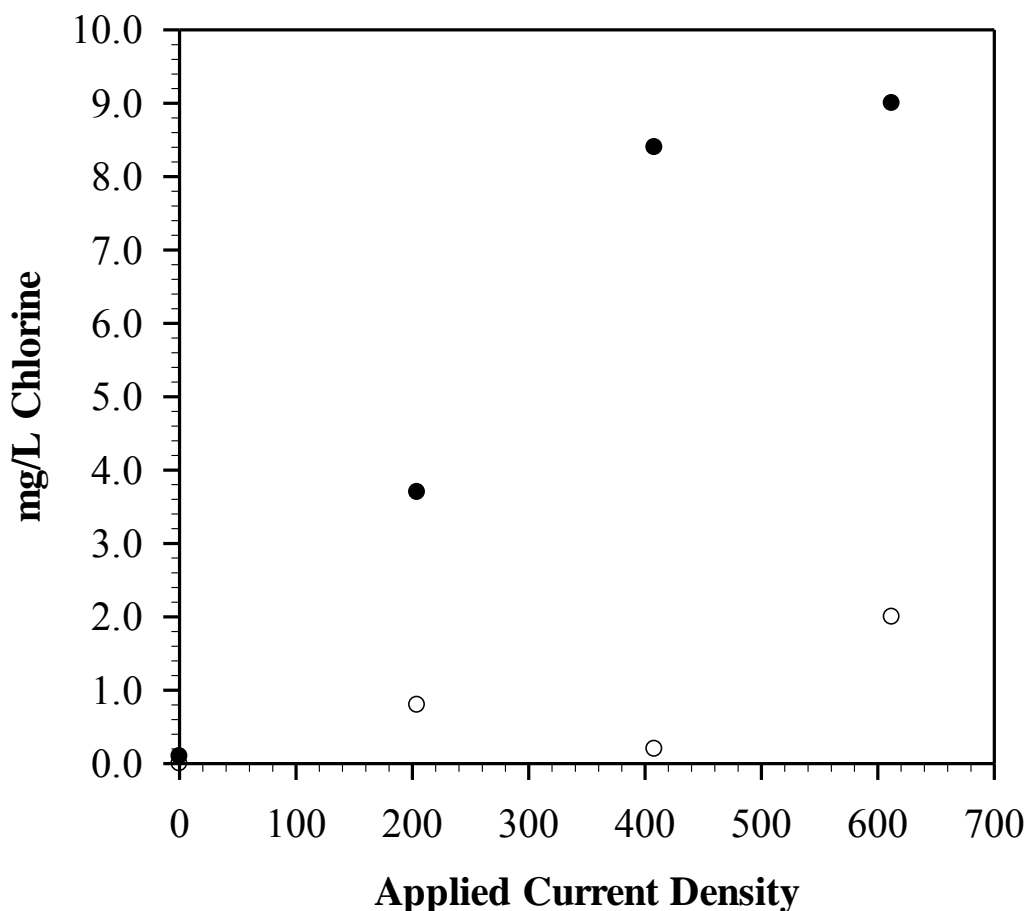
Since the pH of the anode discharge is less than 6 the equilibrium diagram shown in Figure 8 [14] indicates that chlorine primarily exists as hypochlorous acid and does not further dissociate to hypochlorite eq. 20



**Figure 8. Relationship between HOCl and OCl⁻ at various pH values**

A HACH 5870024 pocket coulometer II was used to measure the free chlorine concentration of the combine effluent streams (anode, cathode, and center compartment) from the E-CEM for

three different polarity cycles as a function of applied current density to the E-CEM. The initial concentration of free chlorine in the RO water measured 0.10 mg/L compared to 0.00 mg/L measured for the KW-city water. Figure 9 shows the free chlorine concentration of the combined effluents is the highest for E-CEM effluents produced at the highest current density of 612 A/m<sup>2</sup> applied to the module for both electrode water sources RO (closed symbols, 9 mg/L) and KW-city (open symbols, 2 mg/L).



**Figure 9. Average free chlorine concentration as a function of current density and electrode water source at 60 gpd, (●) RO electrode water source at 612, 408, 204 Amps/m<sup>2</sup> (○) KW-city water electrode water source 612, 408, 204 Amps/m<sup>2</sup>**

As the applied current density to the module is reduced from 612 A/m<sup>2</sup> to 204 A/m<sup>2</sup> the measured free chlorine concentration is reduced from 9 mg/L to 3.7 mg/L RO and 2 mg/L to 0.8 mg/L KW-city water. The effluents produced while using RO water contained on the order of 78% more free chlorine with the exception of measurement made for KW-city water at 408

A/m<sup>2</sup>. The significant increase in free chlorine concentration produced using RO water as the electrode source is contributed to the chloride concentration that is left behind after the desalinization of the seawater by the RO unit. As the RO water passes through the anode the chloride is oxidized at the anode as shown in equation 18. This chloride content also attributes to the higher conductivity measured for this electrode water source. The combined pH of the effluent solutions for each polarity cycle as a function of applied current density measured between 9.7 and 10 (Table 3). At this pH the hypochlorous acid produced at the anode will dissociate to hypochlorite upon mixing of the effluent streams as shown in equation 20.

Since both electrode water sources produced combined effluents measuring far more free chlorine than allowable for discharge by state regulations, methods must be used to reduce the chlorine residual in the anode stream. Based on the operation of outdoor swimming pools, UV light is known to significantly impact free chlorine by photolysis. In a study in which UV disinfection was employed in water chlorinated upstream of the UV disinfection unit, it was reported that the higher the UV dose applied the greater the chlorine dose that was required to keep a fixed chlorine concentration in the effluent water. At the highest UV dose of 4,825 mJ/cm<sup>2</sup> used, the chlorine demand was about five times that obtained without UV light applied [15]. Hypochlorous acid and hypochlorite are photodegraded by UV light as follows:

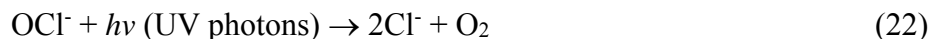
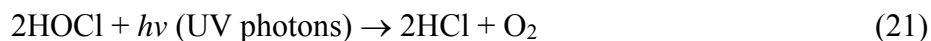
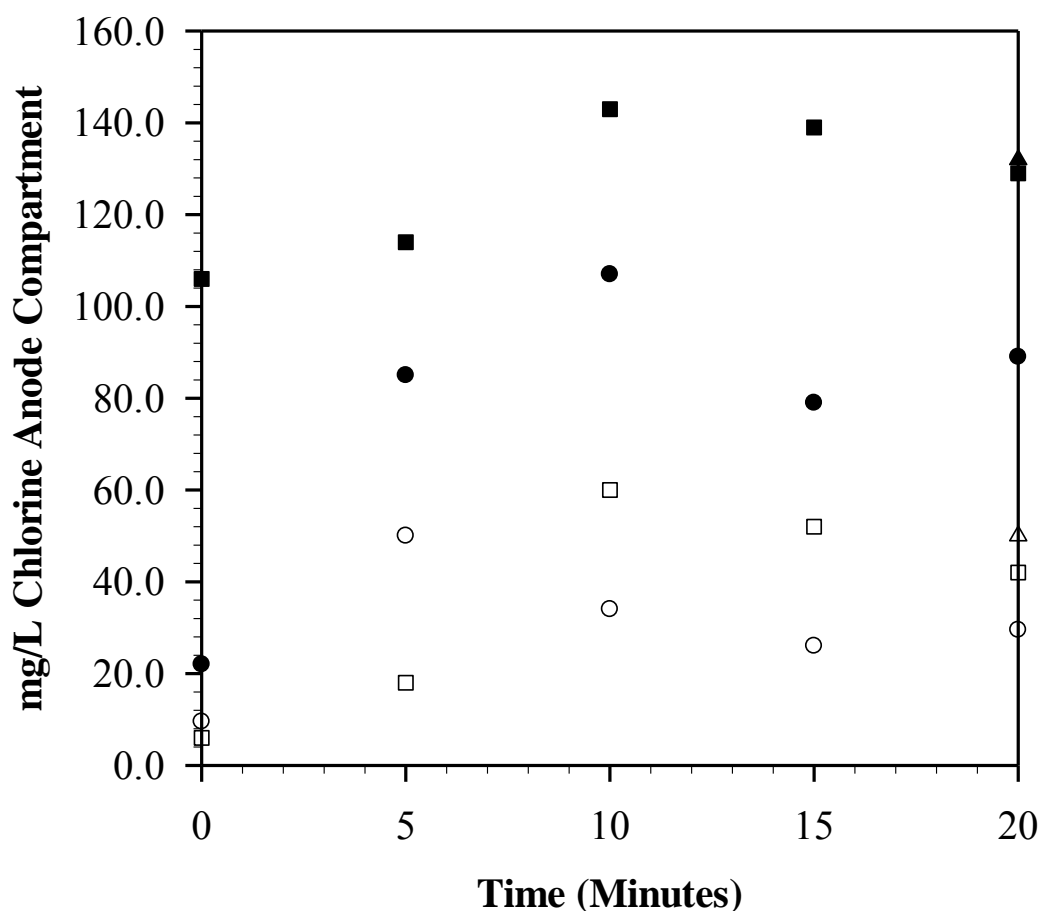


Figure 9 shows the free chlorine concentration of the combined effluents is the highest for E-CEM effluents produced at the highest current density of 612 A/m<sup>2</sup> applied to the module for both electrode water sources RO (closed symbols) and KW-city (open symbols). In these evaluations two different UV sources (750 mJ/cm<sup>2</sup> and 1,500 mJ/cm<sup>2</sup>) were used to treat the anode effluent. Free chlorine was measured every five minutes for four polarity cycles. During two cycles free chlorine was measured without exposure to UV and the average results of these two cycles are compared to the average of two cycles measured after exposure to UV in Figure 10. The average of two polarity cycles run at a flowrate of 60 gpd (227 L/day) produced as high as 107 mg/L of free chlorine and an average of 76 mg/L over a twenty minute cycle (solid circles). At this electrode flowrate the anode was passed through the 750 mJ/cm<sup>2</sup> UV source and the highest free chloride measured was 50 mg/L and the average over a twenty minute cycle (open circles) was reduced by 61% to 30 mg/L.



**Figure 10. Average free chlorine concentration as a function of KW-city electrode flowrate and UV source 60 gpd (●) no treatment (○)UV 750 mJ/cm<sup>2</sup>; 30 gpd (■) no treatment (□) 1,500 mJ/cm<sup>2</sup>; batch 30 gpd (▲) no treatment (Δ) 1,500 mJ/cm<sup>2</sup>**

When the flowrate to the electrode compartments is reduced from 60 gpd (227 lpd) to 30 gpd (113.5 lpd) the average free chlorine measured over the polarity cycles increased by 39% (solid squares). A larger UV source at 1,500 mJ/cm<sup>2</sup> was used to treat the anode effluent and as a result the free chlorine was reduced an average of 72% from 126 mg/L to 36 mg/L over the average of the two polarity cycles (open squares). At the same electrode flowrate of 30 gpd the total anode effluent was collected as a batch over a twenty minute cycle and the free chlorine was measured for the total anode batch solution. The average free chlorine for two cycles measured 132 mg/L (closed triangle). Similarly the free chlorine was reduced by 62% to 50 mg/L after exposure to UV source at 1,500 mJ/cm<sup>2</sup> (open triangle).

These data support that UV treatment of the anode compartment will significantly reduce the chlorine content of the water. Near term evaluations will focus on the treatment of the effluent anode with UV and aerating to determine the effluent chlorine content of the recombined



effluents (anode, cathode, and seawater) from the E-CEM. Electrode flowrates and electrode recycling will be part of the evaluation.

## **7.0 CONCLUSIONS**

In conclusion, two separate evaluations of the E-CEM performance as a function of water composition fed to the electrode compartments of the E-CEM have shown that running KW-city water effects E-CEM performance under standard operating flowrate (60 gpd) conditions to the electrodes. Lowering the standard flowrate from 60 gpd to 9 gpd in the electrode compartments at the highest current density ( $612 \text{ A/m}^2$ ) applied to the E-CEM produces similar electrical efficiencies regardless of the type of water (RO vs KW-city water) fed to the electrode compartments. Changes in the rate in which the E-CEM produces  $\text{CO}_2$  from seawater is shown at the lower current densities using KW-city water as the electrode source. The final combined pH of the effluent is not effected by changing water composition fed to the electrode compartments. Higher discharge pH was found in the colder months of operation as the salinity and temperature of the water is lower.

Quantitative measurements of free chlorine concentration of the combine E-CEM effluent solutions found that using KW-city water lowered the free chlorine concentration by 78%. Preliminary evaluations of the anode effluent found that the free chlorine could be reduced by as much as 60% treating the water with UV light. The effects this treatment will have on the combined effluent is still yet to be determined and will be the subject of near future evaluations.

Finally, these evaluations suggest while using KW-city water as the electrode feed, the E-CEM electrical efficiency can be maintained and the effluent pH and effluent free chlorine can be controlled by changing the individual electrode water flowrates.

## **8.0 MILESTONES**

- Successful demonstration of the E-CEM using KW-city water as the feed to the electrode compartments.
- Successful identification of operating parameters that will maintain E-CEM electrical efficiency and  $\text{CO}_2$  production efficiencies using KW-city water as the feed to the electrode compartments.
- Successful reduction in free chlorine produced at the anode of the E-CEM using KW-city water as the feed to the electrode compartments.
- Successful identification of key hardware and software capabilities that will be added to the future prototype skid to ensure maximum operational flexibility to ensure E-CEM performance while maintaining effluent water quality in terms of pH and free chlorine content.

## 9.0 RECOMMENDATIONS FOR FUTURE STUDIES

After these initial evaluations the following studies are recommended:

- Pursue test and evaluation on total combined effluents from the E-CEM operating at a maximum current density of 612 A/m<sup>2</sup>, minimum flowrate of 9 gpd to the anode, and reduced flowrate to the cathode of 9 to 30 gpd as a function of pH and free chlorine with and without treatment of the anode stream by UV and aerating.
- Pursue test and evaluation of total combined effluents from the E-CEM operating at a maximum current density of 612 A/m<sup>2</sup>, recycling of the anode, and reduced flowrate to the cathode as a function of pH and free chlorine with and without treatment of the anode stream by UV and aerating.
- Ensure modifications made to the E-CEM operating parameters have minimal effect on E-CEM electrical efficiencies and CO<sub>2</sub> production efficiencies.

## 10.0 REFERENCES

- [1] Davis, B. H. Topics in *Catalysis* **2005**, 32, 143-168.
- [2] Olah, G.A., Goeppert, A. Prakash, G.K.S., 2006. Beyond Oil and Gas: The Methanol Economy. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- [3] Willauer, H. D.; DiMascio, F.; Hardy, D. R.; Lewis, M. K.; Williams, F. W. Development of an Electrochemical Acidification Cell for the Recovery of CO<sub>2</sub> and H<sub>2</sub> from Seawater. *Ind. Eng. Chem. Res.* **2011**, 50, 9876-9882.
- [4] Willauer, H. D.; DiMascio, F.; Hardy, D. R.; Williams, F. W. "Extraction of Carbon Dioxide from Seawater by an Electrochemical Acidification Cell Part III: Scaled -Up Mobile Unit Studies (January and April of 2011)" NRL Memorandum Report, 6300-12-9414, 30 May 2012.
- [5] Willauer, H. D.; DiMascio, F.; Hardy, D. R.; Lewis, M. K.; Williams, F. W. Development of an Electrochemical Acidification Cell for the Recovery of CO<sub>2</sub> and H<sub>2</sub> from Seawater II. Evaluation of the cell by Natural Seawater. *Ind. Eng. Chem. Res.* **2012**, 51, 11254-11260.
- [6] Willauer, H. D.; DiMascio, F.; Hardy, D. R.; Williams, F. W. Feasibility of CO<sub>2</sub> extraction from seawater and simultaneous hydrogen gas generation using a novel and robust electrolytic cation exchange module based on continuous electrodeionization technology, *I&EC* **2014**, 53, 12192-12200.
- [7] U.S. Patent 8,658,554 "Catalytic Support For Use In Carbon Dioxide Hydrogenation Reactions" Inventors: Robert W. Dorner, Heather D. Willauer, Dennis R. Hardy; Issued: February 25, 2014.

- [8] U.S. Patent 9,303,323 “Extraction Of Carbon Dioxide And Hydrogen From Seawater And Hydrocarbon Production Therefrom” Inventors: Felice DiMascio, Dennis R. Hardy, M. Kathleen Lewis, Heather D. Willauer, Fredrick W. Williams; Issued: April 5, 2016.
- [9] Willauer, H. D.; DiMascio, F.; Hardy, D. R.; Williams, F. W. Development of an Electrolytic Cation Exchange Module for the Simultaneous Extraction of Carbon Dioxide and Hydrogen Gas from Natural Seawater. *Energy Fuels*, **2017**, *31*, 1723-1730.
- [10] Bradley, M. J.; Ananth, R.; Willauer, H. D.; Baldwin, J. W.; Hardy, D. R.; DiMascio, F.; Williams, F. W. The role of catalyst environment on CO<sub>2</sub> hydrogenation in a fixed-bed reactor. *Journal of CO<sub>2</sub> Utilization*, **2017**, *17*, 1-9.
- [11] Porosoff, M. D.; Baldwin, J. W.; Peng, X.; Mpourmpakis, G.; Willauer, H. D. Potassium-Promoted Molybdenum Carbide as Highly Active and Selective Catalyst for CO<sub>2</sub> Conversion to CO. *ChemSusChem*, **10**, 1-9.
- [12] Johnson, K. M., King, A. E., Sieburth, J. Coulometric TCO<sub>2</sub> Analyses for Marine Studies: An Introduction. *Marine Chem.* **1985**, *16*, 61.
- [13] Riedel, T; Schaub, G.; Jun, K-W; Lee, K-W. Kinetics of CO<sub>2</sub> Hydrogenation on a K-Promoted Fe Catalyst. *Ind. Eng. Chem Res.* **2001**, *40*, 1355-1363.
- [14] Hydro Instruments, Basic Chemistry of Chlorination, <http://www.hydroinstruments.com/files/Basic%20Chemistry%20of%20Chlorination.pdf>, last accessed June **2017**.
- [15] Feng, Y.; Smith, D. W.; Bolton, J. R. Photolysis of aqueous free chlorine species (HOCl and OCl<sup>-</sup>) with 254 nm ultraviolet light. *J. Environ. Eng. Sci.* **2007**, *6*, 227-284.